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   Heriot-Watt University
   Riccarton
   EDINBURGH
   EH14 4AS

   Patents ADP number *(if you know it)* — 05532072001

   If the applicant is a corporate body, give the country/state of its incorporation — UK

4. Title of the invention — Electrochemcial sensor

5. Name of your agent *(if you have one)* — Kennedys Patent Agency Limited

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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   G1 2DT

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Description	10
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KENNEDYS — 1 December 2003

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Simon Black — Tel: 0141 226 6826

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Electrochemical sensor

The present invention relates to an electrochemical sensor apparatus and method and, in particular to an electrochemical sensor that can be used to measure scale, such as mineral scale or other particulates, which deposit on the surface of pipelines or process equipment.

Mineral scale formation is one of the major flow assurance concerns in the chemical industry. The problem of scale build up arises where a fluid is flowing through a pipe or vessel and particulates precipitate out from the fluid and deposit on the surfaces of fluid-carrying equipment. This can cause a blockage to form and the eventual failure of the equipment or disruption in the flow of the fluid.

This problem is particularly apparent in the offshore oil and gas industry. If the formation of scale or other particulate masses goes uncontrolled, the operational safety of the process or plant equipment can be compromised through the failure of subsea safety and flow control valves or other process equipment. If, for

example, a large mass of mineral scale forms in the riser from an oil well, the mass of scale will cause the riser to be blocked, consequently the flow of oil well fluids will be impeded and the pressure will greatly increase, thereby causing the riser to break.

In view of this problem, it is desirable to be able to measure the amount of scale that has formed within a conduit or vessel, and also to be able to estimate and monitor the changes of the scaling potential of a fluid to precipitate out scale or other particulates. A measurement of the surface deposition on control surfaces or changes of scaling tendency will alert the operator. Hence, allows the operator of the well or chemical process to treat the fluid in order to prevent scaling.

Current methods for monitoring the extent of surface scaling and the scaling tendency in reservoirs or pipes have limitations. They tend to involve measuring water or other fluid samples, or to involve the measurement of flow variables such as pressure. These methods do not allow the operator to predict whether scaling will occur. Scale detection often comes too late using this type of monitoring, only after the decrease of the production. In general, efforts to control the scaling problem have concentrated upon strategies to mechanically or chemically remove scale.

It is an object of the present invention to develop an electrochemical sensor that allows the operator to measure the extent of scale formation on a metal surface and to assess the scaling tendency of a fluid.

In accordance with a first aspect of the present invention, there is provided an electrochemical sensor comprising:

an electrical cell having a working electrode;
fluid flow control means, the fluid flow control means being positioned so as to release a fluid jet onto the working electrode, the fluid jet having a predetermined velocity defined by the Reynolds number of the fluid when the fluid is in the fluid flow control means; and
electrical output measurement means
wherein control of the Reynolds number and measurement of the electrical output from the electrical cell provide a measure of the build-up of scale on the working electrode.

Preferably, the electrochemical sensor of the present invention is provided with means for measuring the quantity of scale build up and/or the scaling tendency of the fluid.

Preferably, the electrical output measurement means measures the limiting current response of the electric cell as a function of Reynolds Number.

Preferably, the electrical output measurement means measures the limiting current from an electrochemical tracer as a function of Reynolds number.

Preferably, the apparatus of the present invention further comprises fluid sampling means for obtaining a sample of a test fluid.

Preferably, the fluid sampling means contains fluid isolation means for isolating the test fluid from a bulk fluid.

Preferably, the test fluid isolation means is provided by a container having at least one sealable valve which, when opened, allows the test fluid to enter the sampling means.

Preferably, the fluid flow control means comprises a flow meter connected to a conduit from which said fluid jet is expelled.

Preferably, the electrical cell further comprises a counting electrode and a reference electrode.

In accordance with a second aspect of the present invention, there is provided a method of measuring the scaling potential of a test fluid, the method comprising the steps of:
controlling the velocity of a fluid jet by control of the Reynolds number of said fluid when said fluid is housed in a fluid control means;
releasing the fluid jet from the fluid control means onto a working electrode of an electrical cell; and
measuring the electrical output from the electrical cell as a function of the Reynolds number of the jet fluid, the working electrode being in contact with a sample of the test fluid..

Preferably, the method comprises the further step of isolating the test fluid from a flowing fluid prior to

measuring the electrical output from the electrical cell as a function of the Reynolds number of the fluid.

Preferably, the test fluid is isolated by closing valves arranged upstream and downstream of a predetermined measuring location in a sample measuring means.

It has been found that isolation of a sample of the fluid allows the Reynolds number of the analysing fluid to be carefully controlled by the sensor device.

Preferably the fluid is isolated by removably attaching a sampling conduit to a first conduit in which the bulk of the fluid is situated, and by providing valves to isolate the sampling conduit from the first conduit.

In accordance with a third aspect of the present invention, there is provided a computer program for use with apparatus of the first aspect of the present invention, and with the method of the second aspect of the present invention, in which analysis of the electrical output and the Reynolds number provides information on the quantity of scale build up and/or the scaling tendency of the fluid.

The present invention will now be described by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of an embodiment of the apparatus of the present invention;

Figure 2 is a graph of the limiting current output of the electrochemical cell, as measured against the square root of the Reynolds number of the jet fluid;

Figure 3 is a schematic representation of the second embodiment of the present invention, where the electrochemical cell is positioned in a conduit, removably connected to a riser; and

Figure 4 shows the limiting current correlation with scaling index of the water. The correlation between the supersaturation ratio and the electrochemical measurement make it possible to measure the scaling tendency of the water.

Figure 1 shows an electrochemical sensor setup comprising an electrochemical cell rig 3, having the following components. The electrical cell 3 comprises a working electrode 21 position proximate and normal to the nozzle 9 through which a fluid jet (also known as an impinging jet) exits from the nozzle 9. In addition, the cell rig 18 provides support for a reference electrode 19 and a counting electrode 23 made of platinum, in this example.

The fluid control means consists of a pump 15 positioned downstream of a needle valve 13 which is used to control the flow level of the impinging jet fluid. A flow meter 7 is used to measure the amount of flow of the impinging jet fluid so as to allow calculation of the Reynolds number of the jet fluid. A nozzle 9 provides the means by which the impinging jet fluid exits the fluid control means 5 and contacts the working electrode 21. In this

example, a solution tank is provided for storage and circulation of the impinging jet fluid.

Figure 2 is a graph of the limiting current i_L measured against the square root of Reynolds number ($R_e^{1/2}$). The graph 41 shows three curves. The first curve illustrates a situation in which no scale has been deposited upon the working electrode from the test fluid. Curve 45 illustrates the situation on an unscaled sensor. Curves 46, 47 and 48 illustrate the response from the sensor with 22%, 39% and 46% of scale coverage respectively after immersion for 1, 9 and 24 hours in a scaling solution. These schematic representations clearly show the difference in the limiting current over the same range of Reynolds number, where the level of scaling in the sample is different.

Immersion Time,Hrs	%Scale Coverage
1	22
9	39
24	46

Table 1 shows the resultant scale coverage for different immersion times.

In use, the fluid control means or impinging jet system 5 is submerged in a fluid sample, and is used to control the hydrodynamic regime at the surface of the working electrode 21. Through analysis of the kinetics of the oxygen reduction reaction on the sensor surface, the extent of scaling and the scaling tendency of the fluid can be determined. In this example the test fluid is water.

The potential of the electrochemical sensor 1 is applied to -0.8 volts (with respect to a silver/silver chloride system) when measurements are started. The impinging jet system is then controlled through a range of Reynolds numbers, and the limiting current response is measured as a function of the Reynolds number. Measuring the relationship between these two variables, enables the scaling information to be obtained. In this way, the amount of scale and the scaling tendency of the test fluid can be determined.

Figure 4 shows the limiting current correlation with scaling index of the water (brine) for 6000s. The correlation between the supersaturation ratio and the electrochemical measurement make it possible to measure the scaling tendency of the water.

Figure 3 shows a second embodiment of the present invention, in which the cell rig is installed in the bypass system and the Reynolds number is controlled through valves located in the inlet and outlet of the bypass.

As shown in Figure 3, the bulk fluid 33 flows down conduit 31 and a sample (the test fluid) of the bulk fluid 33 is tapped from the bulk fluid conduit 31 to measurement conduit or bypass system 35. Once the sample of the bulk fluid has been tapped, valves 37 and 39 are closed to enable measurements of the extent of scale or the scaling tendency of the sample to be taken. The impinging jet is directed onto the sample and the fluid surrounding the sensor is essentially static.

The ability to operate the electrochemical sensor of the present invention in situ allows the scaling tendency and scale coverage to be monitored as the pressure, temperature, water chemistry and other environmental conditions change. By locating the apparatus of the present invention within the precise zone of interest within a pipeline, the present invention can monitor the scaling tendency and scale coverage from individual branches of a pipe in, for example, a horizontal well which goes into the main pipeline. Information feedback from the well can provide an early indication of scaling potential problems. Hence, the present invention enables the operator to manage and selectively control individual wells and to inject the correct amount of scale inhibitor in these wells.

Further advantageously, the present invention can detect small amounts of scale and can rapidly (within a matter of 30 minutes or so) determine the scaling tendency of the sample. As a consequence, the operator of the conduit, whether it be a riser from an oil well, a subsea pipeline, a pipe in a desalination plant, or otherwise, can quickly determine the scaling tendency in these positions and can anticipate problems associated with the build up of scale.

In use, the apparatus of the present invention will be connected to an operator terminal by means of a suitable telemetry system. This will allow data to be collected

frequently by the operator using a communications protocol. Real-time data from the oil well or other location will be sent to a PC based surface system that monitors this location. In addition, multiple systems can be used at varying locations in a pipeline system or well or the like, and all of these individual systems can feed data back to a single PC for analysis by the operator, who may then use this data to determine it is necessary to add chemical scale inhibitors to that location, or to otherwise remove or limit the scale measured at that location.

The present invention has a number of advantages over the known prior art. In particular, the present invention allows early measurement of scale or other particulates, and provides a means by which the scaling tendency of the fluid in question can be measured. Measurement of the scaling tendency, as well as the bulk amount of scale, allows the operator to predict the amount of inhibitor that should be used, and also to predict when in the future this inhibitor should be applied.

Improvements and modifications may be incorporated herein, without deviating from the scope of the invention.

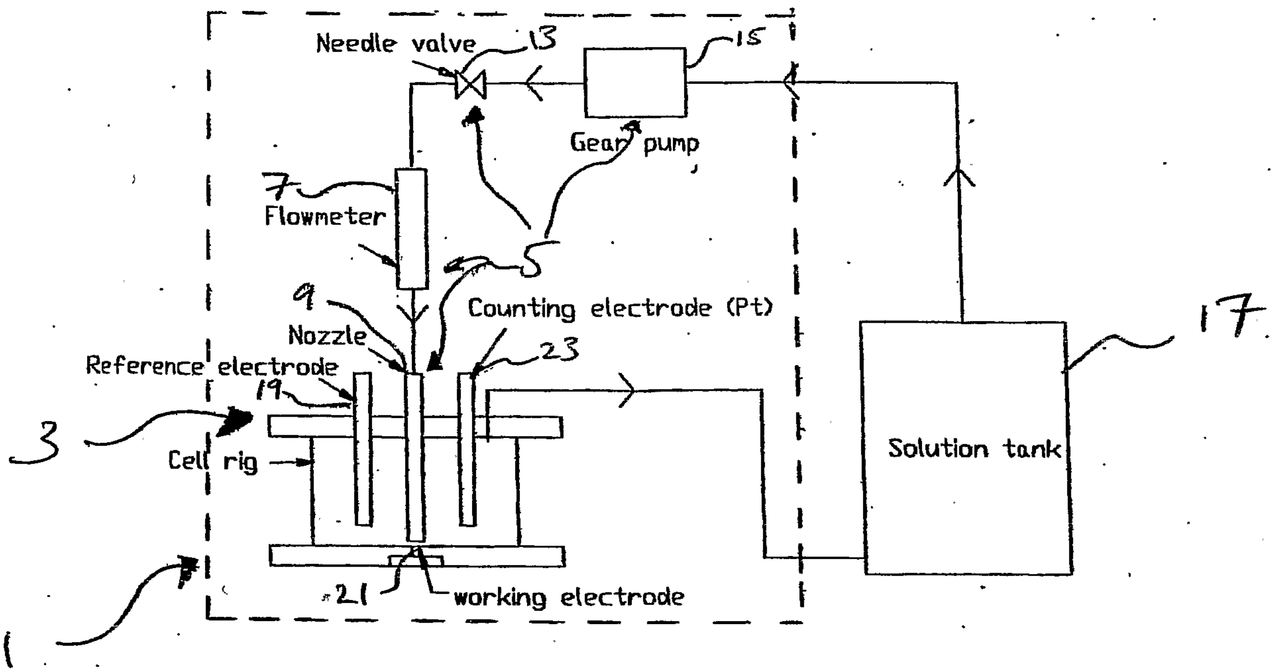
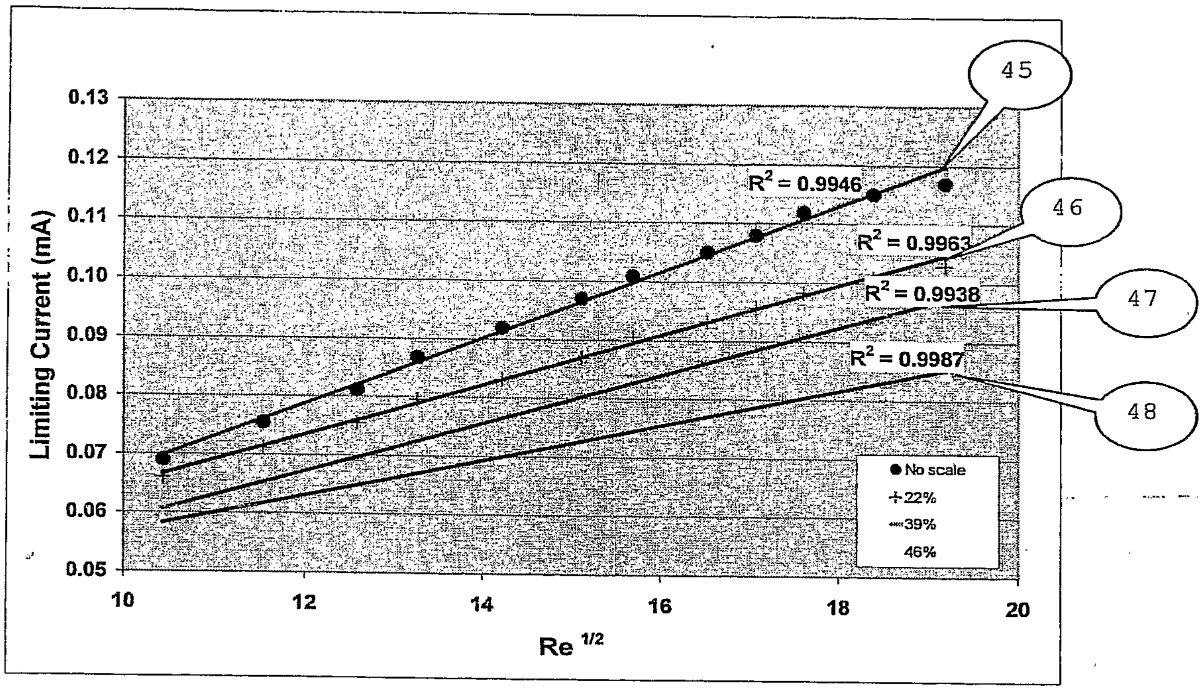

Needle valve
13
15
Gear pump
7
Flowmeter
5
9
Nozzle
Counting electrode (Pt)
23
Reference electrode
19
3
Cell rig
17
Solution tank
1
21
working electrode

FIGURE 1

2/4



45
46
47
48
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
Limiting Current (mA)
R² = 0.9946
R² = 0.9963
R² = 0.9938
R² = 0.9987
No scale
22%
39%
46%
10
12
14
16
18
20
Re 1/2

Figure 2

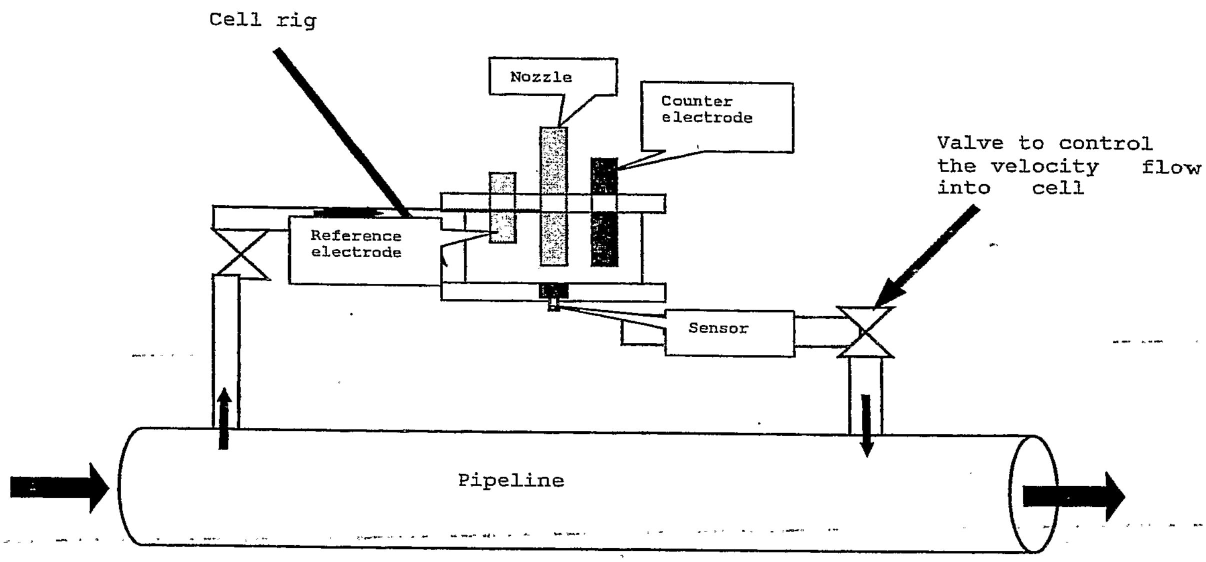

Cell rig
Nozzle
Counter electrode
Valve to control the velocity flow into cell
Reference electrode
Sensor
Pipeline

Figure 3

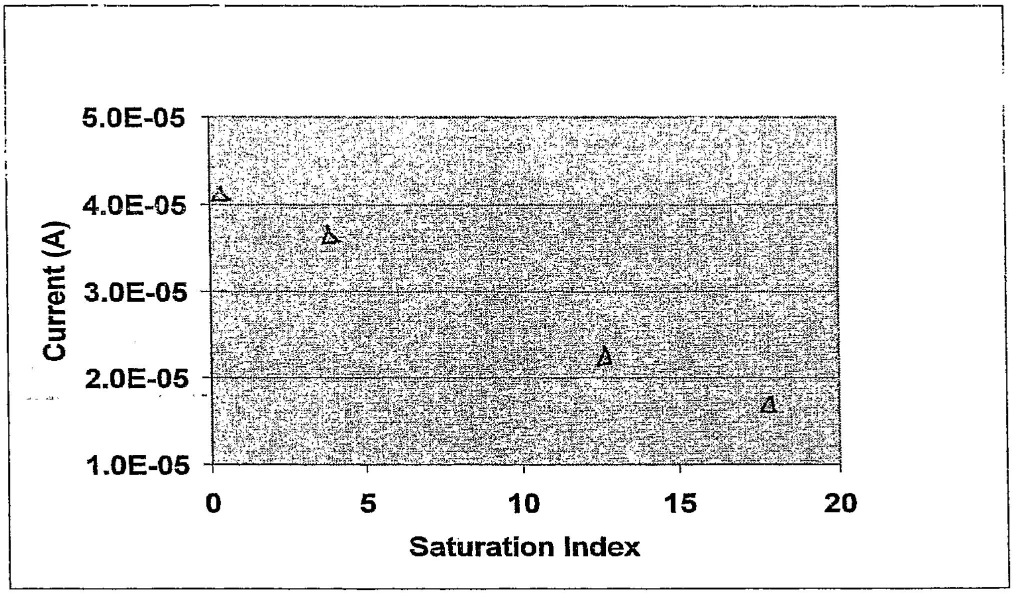

5.0E-05
4.0E-05
3.0E-05
2.0E-05
1.0E-05
Current (A)
0
5
10
15
20
Saturation Index

Figure 4